PLANETARY AERONOMY

I: ABSORPTION AND PHOTOIONIZATION COEFFICIENTS OF PROPYLENE AND BUTENE-1 IN THE VACUUM ULTRAVIOLET

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ABSTRACT   /7265

The total absorption coefficient of propylene and butene-1 vapors in the region from 1500 to 2000 A and the photoionization coefficient in the region 1050 A to the onset of ionization were measured by photoelectric methods. Pressures ranging from 0.04 to 0.2 mm Hg were used for the total absorption coefficient determination, and three pressures from 0.05 to 2 mm Hg were used for the photoionization absorption coefficient determination. Ionization potentials obtained directly for the two vapors agreed with previously published data.

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TABLE OF CONTENTS

ABSORPTION AND PHOTOIONIZATION COEFFICIENTS OF PROPYLENE AND BUTENE-1 IN THE VACUUM ULTRAVIOLET*

I. INTRODUCTION

A continuing program is being conducted to measure the absorption and photoionization coefficients of gases and vapors. The results are applied to planetary atmospheres; suitable fillings for photon counters; and a search for suitable gases which ionize at longer wavelengths than nitric oxide, thereby extending the usable range of absolute measurements.

A detailed analysis of the absorption and photoionization of propylene and butene-1 in the region 1000-2000 Å is given in this report.

The absorption spectrum of propylene and butene-1 below 2000 A has been studied by several investigators. Carr and Stücklen[1] photographed the spectrum of butene-1 vapor down to 1500 A along with several other ethylenic hydrocarbons. They observed a progressive shift towards the visible of the first absorption band of the hydrocarbons with increasing number of substituted alkyl groups. Gary and Pickett[2] made intensity measurements on the absorption of butene-1 down to 1550 A while Price and Tutte[3] photographed the absorption spectra of propylene down to 1100 A. They found the absorption bands in propylene to be rather diffuse; however, they were able to suggest an ionization potential of about 9.6 ev. Watanabe[4] measured the ionization potential

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of propylene and butene-1 using photoelectric methods, and obtained values of 9.73 and 9 58 ev, respectively. By combining a mass spectrometer with a monochromator, Steiner et al.[5] obtained ionization efficiency curves of these two vapors between 1050 A and 1300 A. An ionization potential of 9.73 ev was found for propylene and 9.61 ev for butene. Some recent work on the absorption and photoionization of propylene has been carried out by Schoen and Weissler[6] in the difficult region below 1000 A.

In the present study the total absorption coefficient of propylene and butene-1 vapor in the region 1050 - 2000 A and the photoionization coefficient in the region 1050 A to the onset of ionization were measured by means of photoelectric methods. From these measurements two Rydberg series were identified in propylene along with some vibrational structure. Further, ionization potentials were obtained directly for the two vapors and found to be in good agreement with previously published data.

II. EXPERIMENTAL

Measurements of absorption coefficients and photoionization yields were made by methods described previously.[7][8] Briefly, this method employs a 1-m vacuum monochromator with a resolution of about 1 A, a photomultiplier coated with sodium salicylate as a detector, and an absorption cell placed between the exit slit and the detector. The experimental condtions for the present study were as follows: The light source was a windowless hydrogen discharge tube operated at 0.4 amp dc with about 700 v across the tube; the absorption cell was about 7 cm long and sealed with LiF windows, and was provided with two parallel-plate electrodes, so it also served as an ion chamber; the propylene and butene-1 used was prepared from C.P. grade tank gas by repeated fractional distillation at dry-ice and liquid-nitrogen temperatures. The final purity of these vapors was checked by mass spectrometry which showed that the total impurity present in each gas could not exceed 0.5%.

Data for the total absorption coefficients were obtained with six pressures ranging from 0.04 to 0.2 mm Hg, and for photoionization absorption coefficients with three pressures from 0.5 to 2 mm Hg. Pressures below 0.5 mm Hg were measured with a Consolidated micromanometer, while higher pressures were determined with an oil manometer. Comparatively high pressures were utilized in the case of the photoionization measurements in order to assure total absorption of the radiation within the ion chamber.

The absorption coefficient, k in cm^{-1}, was defined as previously[7] by the equation $I = I_o \exp(-kx)$, where I_o and I are the incident and transmitted light intensities respectively and x, in cm, is the absorbing path length of the vapor expressed at NTP. The photoionization coefficient is defined as the product of the ionization yield and the total absorption coefficient. Absolute yields were obtained by comparison of the ionization current of the investigated vapors to that of nitric oxide. Nitric oxide yields were calibrated against a thermocouple in 1954.[9] These yields have recently been revised[10] and are the ones used in this present work.

III. RESULTS AND DISCUSSION

Mean absorption coefficients of propylene and butene-1 in the spectral region 1050 - 2000 A are summarized in Figures 1-4, which were made by drawing smooth curves through points for about three hundred wavelengths. The experimental uncertainty in the mean k-value is estimated to be about 10% for nearly all wavelengths, pressure measurements being the main source of error.

A. PROPYLENE

1. Region 1500 - 2000 A

Figure 1 gives the total absorption coefficients of propylene between 1500 - 2000 A. A broad absorption band with a maximum at 1720 A is the most prominent feature in this region. Unlike the absorption spectrum of ethylene, which has quite discrete structure, propylene exhibits rather diffuse bands. However, some structure is evident to the short-wavelength side of the absorption band and is possibly due to strong vibrational bands superimposed on the main transition. The average separation of these bands is 1360 cm^{-1} which is of the same order as the separation of the vibrational bands found in ethylene in this region by Price and Tutte,[3] namely, 1370 cm^{-1}. Price and Tutte attribute this vibration in ethylene as being due to the totally symmetrical valence frequency of the double bond.
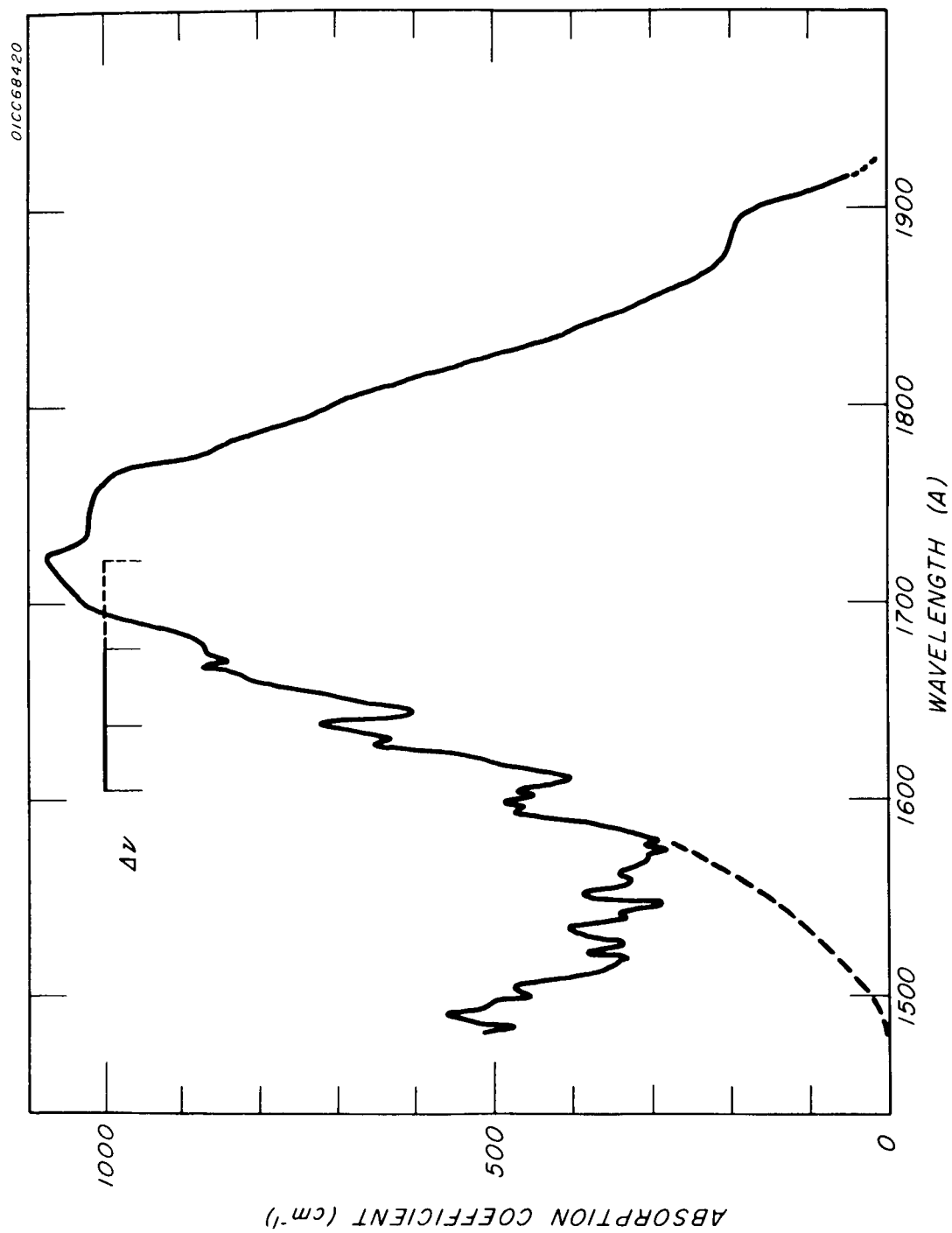
Figure 1. Total absorption coefficients of propylene between 1500 - 2000 A.
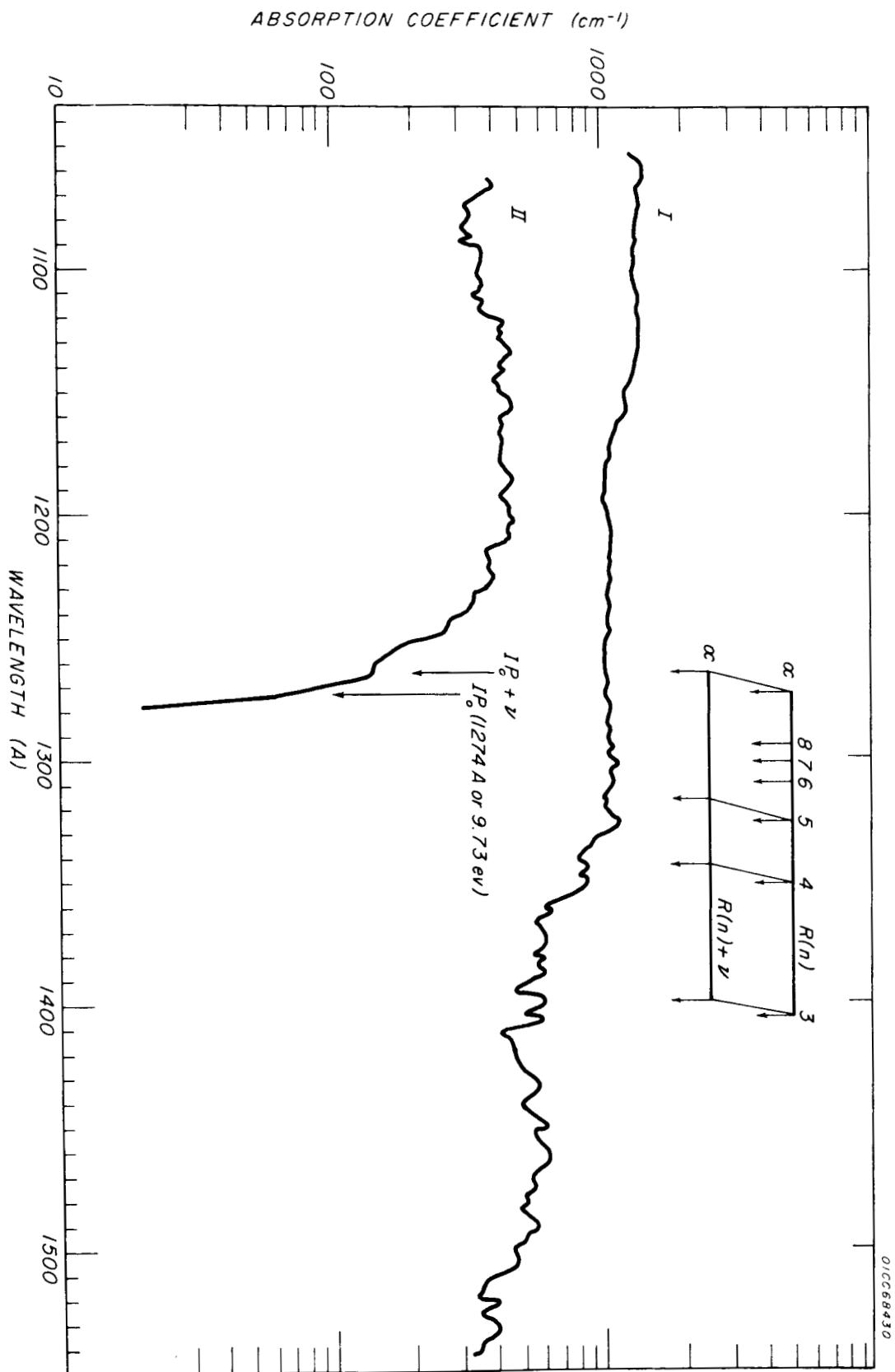
6

Figure 2. Total absorption coefficients (curve I) and photoionization coefficients (curve II) of propylene between 1050 - 1550 A.
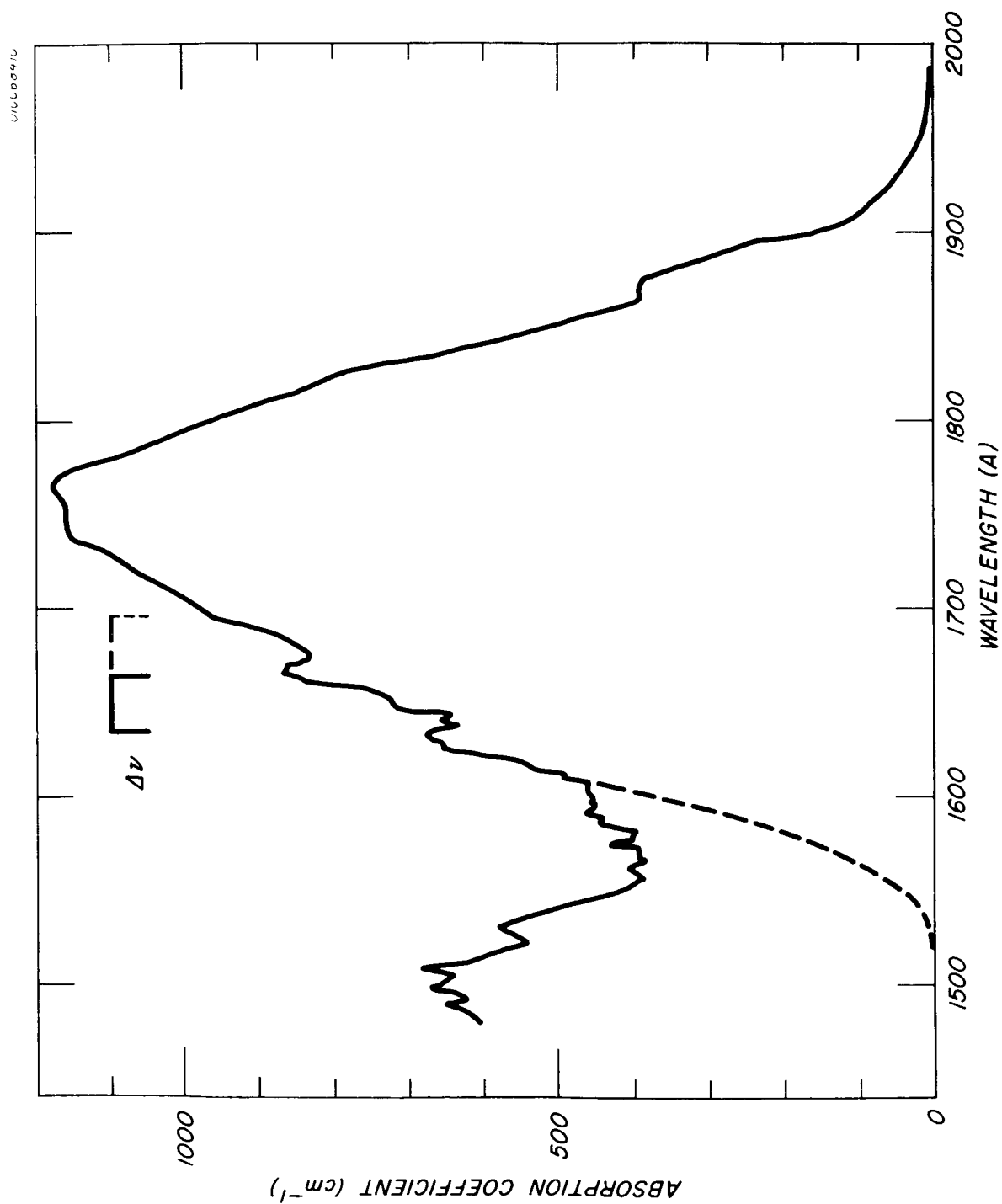
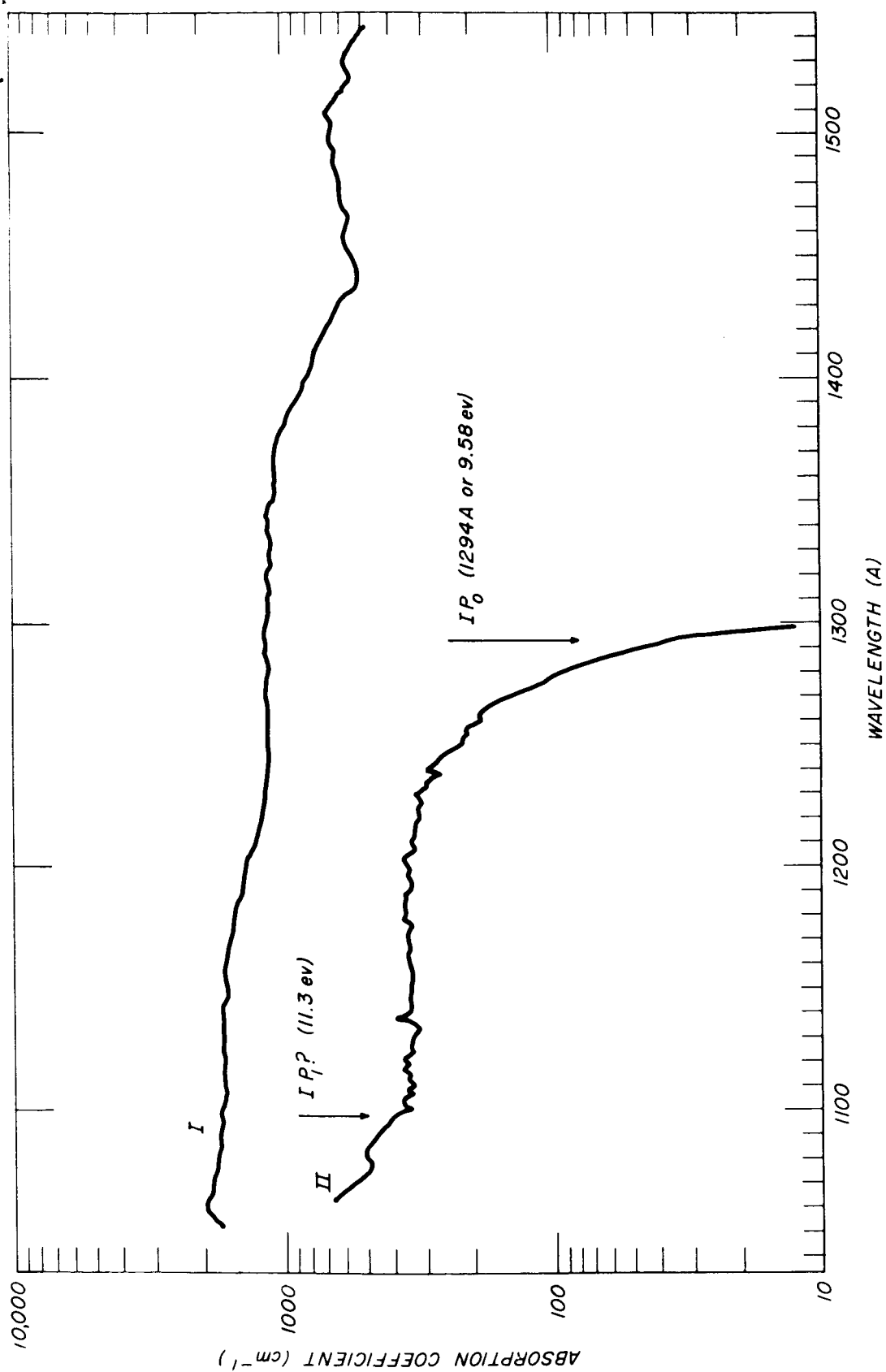Figure 3. Total absorption coefficients of butene-1 between 1500 - 2000 Å.

8

Figure 4. Total absorption coefficients (curve I) and photoionization coefficients (curve II) of butene-1 between 1050 - 1550 A.

9

The oscillator strength f for this absorption band was calculated from the relation $f = 4.31 \times 10^{-9} \int \epsilon d\nu$, where $\epsilon = k/0.1028$.[11] The limits of the integral for the above band are somewhat uncertain to the short-wavelength side of the band; however, the dotted curve in Figure 1 approximates the band limit. Taking the area under this curve one gets $f = 0.32$.

2. Region 1050-1500 A.

To wavelengths shorter than 1300 A the absorption spectrum, curve I, Figure 2, is essentially continuous. However, between 1300 - 1550 A considerable structure can be seen. Although this structure is more diffuse than in ethylene, two Rydberg series can be identified with the help of the photoionization absorption coefficient curve (II). This curve gives an onset for ionization at 1274 A (9.73 ev), while a second break in the curve is indicative of another ionization potential due to a transition into a vibrational state of the ion, $\Delta\nu = 527 \text{ cm}^{-1}$, at 1265.5 A (9.80 ev). This vibration probably represents a twisting vibration about C = C bond in analogy with the almost certain identification of this vibration in ethylene.[3] Using these ionization potentials as a guide and from the doublet nature of some of the bands in curve I, two series were identified and found to fit the following Rydberg formulas:

$$R(n): \qquad \nu = 78586 - R/(n+0.85)^2 \quad n = 3, 4 \ldots, \qquad (1)$$

$$R(n) + \Delta\nu: \quad \nu = 79051 - R/(n+0.85)^2 \quad n = 3, 4 \ldots, \qquad (2)$$

10

where R is the Rydberg constant, $R(n)$ a Rydberg series, and $R(n) + \Delta\nu$ a doublet member of the $R(n)$ series. The position of these Rydberg bands are shown in Figure 2. The wave numbers of the observed bands and those computed from Equations (1) and (2) agree well and are shown in Table I. The calculated series limits of 78 586 cm^{-1} (9.74 ev) and 79 051 cm^{-1} (9.80 ev) agree well with the ionization potentials obtained from the photoionization experiments.

The identification of the absorption bands as Rydberg bands appears highly probable; however it would be desirable to perform a similar experiment using fully deuterated propylene. In this case, the bands forming the above series would be expected to be shifted slightly towards short-wavelengths in going from C_3H_6 to C_3D_6.

The structure of curve II compares favorably with that published by Steiner et al.[5] In particular, they obtain an ionization potential at 9.73 $\pm$ 0.02 ev and a break in their ionization efficiency curve occurs at the same position we have assigned to the $R + \nu$ series limit at 9.80 ev. The observed ionization potential at 9.73 ev agrees with previously published data using photoionization methods.[4]

Price and Tutte[3] did not publish a Rydberg series in propylene, however, from the structure of their spectrum they do estimate a series limit at 9.6 ev in good agreement with the first series limit of 9.74 ev found in this work. Electron impact techniques yield, in general, slightly higher ionization potentials than photoionization methods, and in propylene these values vary from 9.81 to 10 ev.[12]

11

TABLE I

RYDBERG BANDS FOR PROPYLENE IN CM^{-1}

	R(n)		R(n) $\cdot$ ν	
n	ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}
3	71 120	71 183	71 430	71 648
4	73 910	73 921	74 380	74 386
5	75 360	75 379	75 930	75 844
6	76 250	76 247		
7	76 800	76 805		
8	77 190	77 188		
∞		78 586		79 051

Theoretical values at 10.14 and 9.96 ev for the first ionization potential of propylene have been calculated by Higuchi[13] and Streitwieser,[14] respectively. Walsh[15] has estimated that a second ionization potential, corresponding to the removal of a σ CC electron, should occur around 12.0 ev. This occurs at shorter wavelengths than reported here and no evidence of its presence is apparent from curve II; however, due to the lowering of the ionization potentials by alkyl substitution it may be apparent in butene.

B. BUTENE-1

1. Region 1500 - 2000 A

Butene-1 has a very similar absorption spectrum to that of propylene, however, as can be seen from Figure 3 the discrete structure is much more diffuse. The maximum of the main absorption band at 1760 A shows a shift towards the red as compared to propylene. This shift was also observed by Carr and Stücklen[1] as the number of alkyl groups around the double bond increased.

An f value of 0.36 was obtained assuming the band followed the dotted curve in Figure 3. This value compares favorably with that of 0.39 obtained by Gary and Pickett.[2]

2. Region 1050 - 1500 A

In Figure 4, curve I, some absorption bands can be seen between 1300 and 1550 A; however, they are far too diffuse and unresolved to observe any Rydberg series. The absorption spectrum is other-

13

wise continuous down to the limit of observation at 1050 A.

Curve II in Figure 4 represents the photoionization absorption coefficient of butene-1. Ionization begins at about 1297 A, rises sharply, and has a point of inflection at 1294 A or 9.58 ev representing the first ionization potential of the molecule. The region between 1297 and 1294 A represents the Boltzmann energy distribution in the molecule at room temperature. The ionization potential at 9.58 ev is in good agreement with previously published data using photoionization methods,[4][5] and is in general slightly lower than values obtained by electron impact techniques, which vary from 9.76 to 10.00 ev.[12] Franklin calculated the ionization potential of butene-1 using a semi-empirical relation and obtained a value of 9.7 ev.[16] As mentioned in the discussion on propylene, Walsh[15] estimated a higher ionization potential in propylene at around 12 ev. Due to the lowering of the ionization potential by alkyl substitution one might expect a higher ionization potential in butene-1 at somewhat less than 12.0 ev. From curve II, Figure 4, an abrupt increase in the ionization cross section at 11.3 ev suggests a higher ionization potential and may be due to the removal of the σ CC electron as suggested by Walsh.

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